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Symplectic Algorithms of Molecular Dynamics. An Application to the United-Residue Model.

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In order to describe the dynamics of a molecular system, governed by an effective Hamiltonian based on a coarse-grain United-Residue (UNRES) potential energy model[1], multiple time-step (MTS) symplectic algorithms have been developed and implemented. The theoretical background of symplectic flows generated by the Hamiltonian equations of motions is outlined and the principles of symplectic integrators are presented. Decomposition of the UNRES forces was proposed, and an optimal MTS scheme for real molecular systems has been implemented. This algorithmic approach appeares to be optimal for the UNRES model, which results in a noticeable speed up of computations. Taking advantage of the reduced model and the MTS algorithmic approach, one can carry out long-time MD simulations. The results are being prepared for publication[5].

1 Hamiltonian Systems

Among many ordinary differential equation (ODE) systems, Hamiltonian systems are of particular importance in physics. The hamiltonian equations of motion are:

$$\dot{q}_i = \frac{\partial H}{\partial p_i} \ , \ \dot{p}_i = -\frac{\partial H}{\partial q_i} \tag{1}$$

The phase-flow given by such a system conserves the Hamiltonian function (energy). In general, the Hamiltonian systems conserve the so-called symplectic structure (the symplectic structure is defined as a quadratic differential form, providing $d\omega^2 = 0^2$), therefore a series of values expressed by Poincaré integrals, e.g.:

$$\oint_{C(0)} \sum_i p_i dq_i = \oint_{C(t)} \sum_i p_i dq_i, \tag{2}$$

where $C(t)$ is an arbitrary closed curve in the phase space evolving from the initial state $C(0)$ according to the flow.

2 Integration of the Hamiltonian Systems.

An algorithm for integration of the Hamiltonian systems[4] should conserve the symplectic structure with the phase-flow. It also conserves a modified, approximate Hamiltonian: $H^S = H + \tilde{H}$ which is located near the original one. In order to derive the symplectic algorithms one can use the Liouville operator (Poisson bracket) acting on the state vector to denote the Hamilton equations:

$$\dot{\mathbf{\Gamma}} = \hat{L} \begin{pmatrix} \mathbf{q} \\ \mathbf{p} \end{pmatrix}, \tag{3}$$

with the formal solution for a time interval Δt:

$$\mathbf{\Gamma}(t + \Delta t) = e^{\Delta t \hat{L}} \mathbf{\Gamma}(t). \tag{4}$$

Application of the Trotter factorization scheme and time dicretisation give the recipe for the Velocity Verlet algorithm:

$$\mathbf{\Gamma}(t + \Delta t) \approx e^{\frac{\Delta t}{2}\hat{L}_U} e^{\Delta t \hat{L}_T} e^{\frac{\Delta t}{2}\hat{L}_U} \mathbf{\Gamma}(t), \tag{5}$$

where the $\hat{L} = \hat{L}_T + \hat{L}_U$ is decomposed into parts related to the kinetic energy and potential energy, respectively. The symplecticity of such an algorithm depends on the time-step Δt

3 Multiple Time-Step Algorithms.

In order to achieve the Multiple Time-Step (MTS) scheme for integrating the Hamilton equations of motion it is necessary to decompose the potential part of Liouville operator, into two parts: one generates the fast varying forces and the other one the slow varying forces:

$$\hat{L}_V = \hat{L}_{Vf} + \hat{L}_{Vs}. \tag{6}$$

Now we can construct the scheme which gives the family of MTS algorithms, each for different splitting number N:

$$\mathbf{\Gamma}(t + \Delta t) \approx e^{\frac{\Delta t}{2}\hat{L}_{Vs}} \left(e^{\frac{\Delta t}{2N}\hat{L}_{Vf}} e^{\frac{\Delta t}{N}\hat{L}_T} e^{\frac{\Delta t}{2N}\hat{L}_{Vf}} \right)^N e^{\frac{\Delta t}{2}\hat{L}_{Vs}} \mathbf{\Gamma}(t). \tag{7}$$

Now the symplecticity of a given algorithm depends on the splitting number N and time-step Δt.

4 Application of the MTS Algorithm to UNRES Model.

The United-Residue force field model describes a polypeptide chain in a reduced and physics-based approach. Residues are represented by α-carbon atoms, which are linked together by virtual bonds - this constitutes the backbone. The representation of the side chains is united, and it is referred to the C^α atoms. The interaction sites are located in the midpoints between consecutive C^α (the backbone) and at given distances from C^α atoms (the side chains).

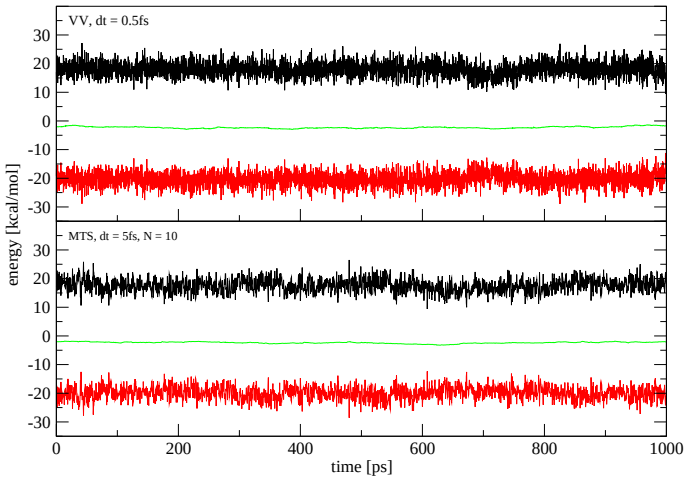

Figure 1. Energies obtained using the Velocity Verlet and MTS algorithms. The potential energy - lower line, total energy - middle line and kinetic energy - upper line, on each graph. The simulation was carried out for the Ala_{10}.

The UNRES potential function was decomposed into parts generating slow and fast varying forces. Based on this, the MTS algorithm was implemented[3,5] and tested with several integration schemes - different pairs $(N, \Delta t)$, see Fig. 1, for example.

The Velocity Verlet algorithm and MTS algorithm gives the same stability of the MD run. The computational cost of performing equivalent MD runs is much lower when using the MTS algorithm, which is shown in Table 1:

Table 1. Values for the maximum amplitude of the energy fluctuation from the Ala_{10} 1 nano second MD run. Time step units are in mtu.(1mtu = 48.9fs), and energy in kcal/mol.

Velocity Verlet			MTS			
Δt	$\lvert\delta E\rvert$	Exec. time	Δt	N	$\lvert\delta E\rvert$	Exec. time
0.01	1.50	79.8 min	0.1	10	1.42	9.23 min

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